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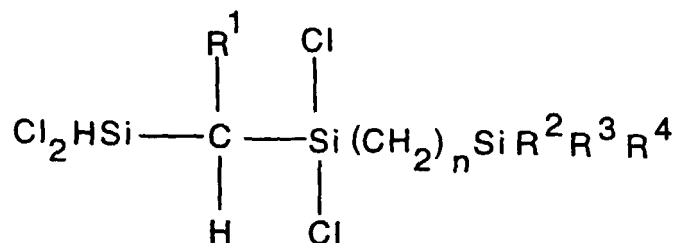
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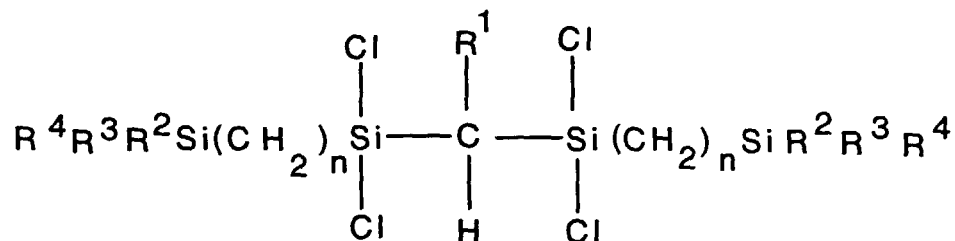
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(54) **Silicon compounds containing silamethylene bonds and method for their preparation**

(57) The present invention is organosilicon compounds described by formula (1)



and formula (2)



were R¹ is selected from hydrogen, dichlorosilyl, trichlorosilyl, methyldichlorosilyl, dimethylchlorosilyl or trimethylsilyl, each R², R³ and R⁴ are independently selected from hydrogen, chlorine and alkoxy radicals having 1 to 12 carbon atoms, aryloxy radicals having up to 12 carbon atoms, aryl radicals having up to 12 carbon atoms or saturated hydrocarbon radicals having 1 to 12 carbon atoms, n=2 to 6 and methods for the making of organosilicon compounds described by formulas (1) and (2).

Description

[0001] The present invention is an organosilicon compound having silamethylene bonds and methods for their preparation by a hydrosilation reaction. Since the description of hexachloroplatinic acid as a catalyst for hydrosilation in 1957 by Speier et al., hydrosilation has become one of the fundamental methods for synthesizing organosilicon compounds. Speier et al., J. Am. Chem. Soc. 1957, 79, 974. In the hydrosilation process Si-H bond containing silicon compounds are reacted and added to multiple bonds of organic compounds such as carbon-carbon, carbon-oxygen, carbon-nitrogen, nitrogen-nitrogen and nitrogen oxygen.

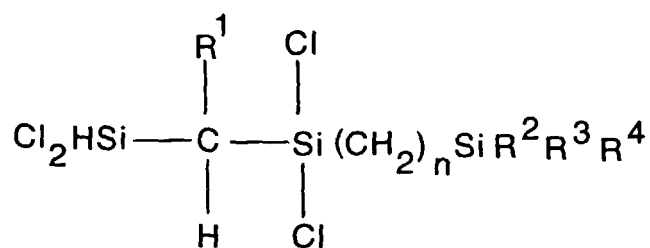
[0002] Yeon et al., J. Organomet. Chem. 1996, 516, 91, reported in 1996 the direct synthesis of Si-H containing bis(silyl)methanes by reacting silicon metal with a mixture of methylene chloride and hydrogen chloride.

[0003] Jung et al., U.S. Patent 5,399,740, describe the reaction of silicon metal with a mixture of dichloromethyl group containing silane and hydrogen chloride to obtain tris(silyl)methanes in moderately high yield.

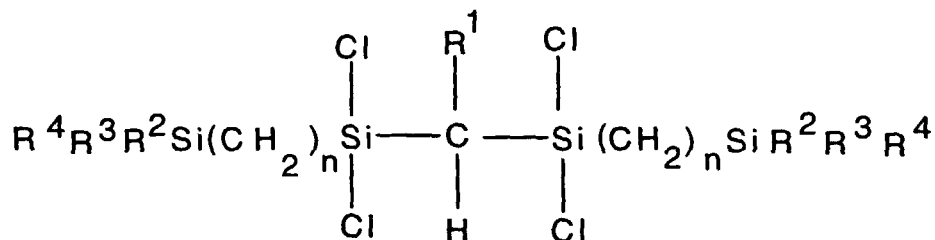
[0004] Han et al., Organometallics 1997, 16, 93, reported the direct synthesis of Si-H containing tris(silyl)methanes by reacting silicon metal with a mixture of chloroform and hydrogen chloride.

[0005] The organosilicon compounds of the present invention are useful, for example, as intermediates for forming silicon carbides by pyrolysis.

[0006] The present invention is an organosilicon compounds described by formula (1)



and formula (2)



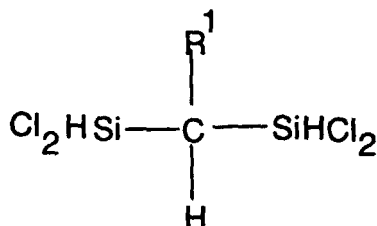
where R^1 is selected from hydrogen, dichlorosilyl, trichlorosilyl, methyldichlorosilyl, dimethylchlorosilyl or trimethylsilyl, each R^2 , R^3 and R^4 are independently selected from hydrogen, chlorine and alkoxy radicals having 1 to 12 carbon atoms, aryloxy radicals having up to 12 carbon atoms, aryl radicals having up to 12 carbon atoms or saturated hydrocarbon radicals having 1 to 12 carbon atoms, $n=2$ to 6; and methods for the making of organosilicon compounds described by formulas (1) and (2).

[0007] In formulas (1) and (2) each R^2 , R^3 and R^4 can be, for example, hydrogen, chlorine, methoxy, ethoxy, phenoxy, methyl, ethyl, tert-butyl, cyclopentyl, cyclohexyl, phenyl, chlorophenyl and chloromethyl. In formulas (1) and (2) it is preferred that each R^2 , R^3 and R^4 be independently selected from hydrogen, chlorine or methyl.

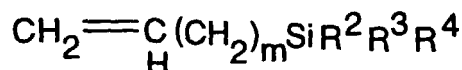
[0008] In formulas (1) and (2), $n=2$ to 6 and in formula (2) each n can be the same or different value. Preferred is where in formulas (1) and (2), $n=2$ or 3 and in formula (2) each n is the same value.

[0009] Preferred organosilicon compounds within the scope of formulas (1) and (2) are selected from 1,1,3,3,6,6-hexachloro-1,3,6-trisilaheptane; 2,2,5,5,7,7,10,10-octachloro-2,5,7,10-tetrasilaundecane; 1,1,1,4,4,6,6-heptachloro-1,4,6-trisilaheptane; 1,1,1,4,4,6,6,9,9,9-decachloro-1,4,6,9-tetrasilanonane; 1,1,1,3,3,6,6-heptachloro-2-dichlorosilyl-1,3,6-trisilaheptane; 1,1,1,3,3,6,6,6-octachloro-2-dichlorosilyl-1,3,6-trisilaheptane; 2,2,4,4,7,7-hexachloro-3-dichlorosilyl-2,4,7-trisilaheptane; and 2,2,4,4,7,7,7-heptachloro-3-dichlorosilyl-2,4,7-trisilaheptane.

[0010] The present invention is also a method for making organosilicon compounds described by formulas (1) and (2). The method comprises effecting hydrosilation of a bis(dichlorosilyl)methane described by formula (3)



with an unsaturated organosilane described by formula (4)



in the presence of an effective amount of hydrosilation catalyst, where R^1 , R^2 , R^3 and R^4 are as previously described and $m=0$ to 4. In a preferred method $m=0$.

[0011] Preferred examples of the bis(dichlorosilyl)methane include bis(dichlorosilyl)methane, bis(dichlorosilyl)trichlorosilylmethane and bis(dichlorosilyl)dichloromethylsilylmethane.

[0012] Preferred examples of the unsaturated organosilane include dichloromethylvinylsilane and trichlorovinylsilane.

[0013] In the method, the mole ratio of the unsaturated organosilane to the bis(dichlorosilyl)methane can be within a range of 0.1 to 10. It is preferred that the mole ratio of the unsaturated organosilane to the bis(dichlorosilyl)methane be within a range of 0.5 to 2. It is preferred that the mole ratio of unsaturated organosilane to the bis(dichlorosilyl)methane be within a range of 0.5 to 1.5 when the desired product is described by formula (1) and within a range of 0.75 to 2 when the desired product is described by formula 2.

[0014] The present method requires the presence of an effective amount of a metallic hydrosilation catalyst. The metallic hydrosilation catalyst can be any such catalyst which is known to catalyze the reaction of silicon-bonded hydrogen atoms with silicon-bonded alkenyl groups. The preferred metallic hydrosilation catalyst for use in the present method are platinum group metal-containing catalyst. By "platinum group metal", it is meant ruthenium, rhodium, palladium, osmium, iridium and platinum. Examples of platinum group metal-containing catalyst which may be useful in the present method are found in, for example, Willing, U.S. Patent 3,419,593; Lee et al., U.S. Patent 3,989,668; Chang et al., U.S. Patent 5,036,117; Ashby, U.S. Patent 3,159,601; Lamoreaux, U.S. Patent 3,220,972; Chalk et al., U.S. Patent 3,296,291; Modic, U.S. Patent 3,516,946; Karstedt, U.S. Patent 3,814,730 and Chandra et al., U.S. Patent 3,928,629 which show useful platinum group metal-containing catalyst and methods for their preparation. A preferred platinum group metal is platinum. The preferred platinum group metal catalysts are compounds and complexes of platinum. Examples of metallic hydrosilation catalysts which may be useful in the present method include H_2PtCl_6 , H_2PtCl_6 in solution in isopropyl alcohol (IPA), H_2PtCl_6 /IPA/ PPh_3 solutions, $Pt(PPh_3)_4$, $Pt(CH_2=CH_2)(PPh_3)_2$, $RhCl(PPh_3)_3$, $Pd(PPh_3)_4$ and $Ni(PEt_3)_4$; where Et is ethyl and Ph is phenyl. The preferred catalyst for use in the present invention is an isopropyl alcohol solution of H_2PtCl_6 .

[0015] The present method requires that an effective amount of a metallic hydrosilation catalyst be added. By the term "effective amount", it is meant an amount of catalyst sufficient to accelerate a reaction between the silicon-bonded hydrogen atoms of the bis(dichlorosilyl)methane and the unsaturated organosilane. Generally, an effective amount of the metallic hydrosilation catalyst is an amount with a range of 1×10^{-5} to 0.05 moles of metal per mole of the bis(dichlorosilyl)methane.

[0016] The method of effecting hydrosilation of the bis(dichlorosilyl)methane with the unsaturated organosilane can be any of those known methods for effecting hydrosilation reactions in the presence of a metallic hydrosilation catalyst. In a preferred process an optional organic solvent, the bis(dichlorosilyl)methane and the metallic hydrosilation catalyst are placed in a reactor under an inert atmosphere such as dried nitrogen. The unsaturated organosilane is then slowly added to the reactor with stirring. After addition of the unsaturated organosilane, the reactor content may be further heated at a temperature from 10°C. to 150°C. for a time sufficient to ensure completion of the hydrosilation reaction. It is preferred to heat the reactor content at a temperature within a range of 20°C. to 150°C., and even more preferred is a temperature of 25°C. to 110°C. The length of time the reactor content is heated to effect the hydrosilation reaction will depend upon the reactants and the temperature to which the reactor content is heated. Generally a time of 0.5 hours to 20 hours is useful, with a heating time of 1 hour to 5 hours being preferred.

[0017] The use of an organic solvent in the present method is optional. Organic solvents which may be useful in the

present method include benzene, toluene, xylene, chlorobenzene and anisole. The organic solvent may be added as a diluent in any amount that preferably does not dilute the reactants to a point that detrimentally effects the reaction rate and yield.

[0018] The following examples are provided to illustrate the present invention. These examples are not intended to limit the scope of the claims herein.

Example 1

[0019] Hydrosilation of dichloromethylvinylsilane with bis(dichlorosilyl)methane. To a 250 ml flame dried flask equipped with a magnetic stirrer and reflux condenser was added 85 g of bis(dichlorosilyl)methane and 200 μ l of 0.1 M H_2PtCl_6 /IPA solution and the flask placed under a dry nitrogen atmosphere. Then, to the flask was added 42.1 g of dichloromethylvinylsilane and the flask content stirred for 40 minutes. The temperature of the flask content was then increased to 90°C. and stirring continued for 2 hours. The flask content was vacuum distilled at 67 Pa to yield 91.8 g of 1,1,3,3,6,6-hexachloro-1,3,6-trisilaheptane; 1H -NMR ($CDCl_3$, ppm): 0.85 (s, 3H, $SiCH_3$), 1.23-1.48 (m, 6H, $SiCH_2SiCH_2CH_2Si$), 5.71 (s, 1H, SiH). The distillation residue was recrystallized with hexane to give 16.2 g of 2,2,5,5,7,7,10,10-octachloro-2,5,7,10-tetrasilaundecane as colorless needle-type crystals; 1H -NMR ($CDCl_3$, ppm) : 0.81-0.84 (s, 6H, $SiCH_3$), 1.23-1.38 (m, 10H, $SiCH_2CH_2SiCH_2Si$).

Example 2

[0020] Hydrosilation of trichlorovinylsilane with bis(dichlorosilyl)methane. In the same apparatus as described in Example 1, 3.3 g of bis(dichlorosilyl)methane, 20 ml of dried benzene and 60 μ l of 0.1 M H_2PtCl_6 /IPA solution were placed and the flask placed under a dry nitrogen atmosphere. Then, to the flask were added 1.2 g of trichlorovinylsilane and the flask content stirred for 5 minutes. The flask content was refluxed with stirring for 2 hours. Then, the flask content was vacuum distilled at 67 Pa to give 3.4 g of a mixture comprising 1,1,1,4,4,6,6-heptachloro-1,4,6-trisilahexane (TCD- GC area of 69.7%) (TCD-GC = thermal conductivity detection-gas chromatography) and 1,1,1,4,4,6,6,9,9,9-decachloro-1,4,6,9-tetrasilanonane (TCD-GC area 3.7%). 1,1,1,4,4,6,6-Heptachloro-1,4,6-trisilahexane: 1H -NMR ($CDCl_3$, ppm): 1.35-1.57 (m, 6H, $SiCH_2SiCH_2CH_2Si$) 5.71 (s, 1H, SiH). 1,1,1,4,4,6,6,9,9,9-Decachloro-1,4,6,9-tetrasilanonane: 1H -NMR ($CDCl_3$, ppm): 1.26-1.53(m, 10H, $CH_2CH_2SiCH_2SiCH_2CH_2$).

Example 3

[0021] Hydrosilation of dichloromethylvinylsilane with bis(dichlorosilyl)trichlorosilylmethane. In the same apparatus as described in Example 1, 2.5 g of bis(dichlorosilyl)trichlorosilylmethane, 20 ml of dried benzene and 40 μ l of 0.1 M H_2PtCl_6 /IPA solution were placed. Then, to the flask was added 0.5 g of dichloromethylvinylsilane and the flask content stirred for 5 minutes. The flask content was refluxed with stirring for 2 hours. Then, the flask content was vacuum distilled at 67 Pa to give 1.7 g of a mixture comprising 1,1,1,3,3,6,6-heptachloro-2-dichlorosilyl-1,3,6-trisilaheptane (TCD-GC area 75.1%); 1H -NMR ($CDCl_3$, ppm): 0.84 (s, 3H, $SiCH_3$), 1.27-1.33, 1.46-1.56 (m, 4H, $SiCH_2CH_2Si$), 1.85 (s, 1H, SiH) 5.89 (s, 1H, SiH).

Example 4

[0022] Hydrosilation of trichlorovinylsilane with bis(dichlorosilyl)trichlorosilylmethane. In the same apparatus as described in Example 1, 2.5 g of bis(dichlorosilyl)trichlorosilylmethane, 20 ml of dried benzene and 50 μ l of 0.1 M H_2PtCl_6 /IPA solution were placed. Then, to the flask was added 0.58 g of dichloromethylvinylsilane and the flask content stirred for 5 minutes. The flask content was refluxed with stirring for 2 hours. Then, the flask content was vacuum distilled at 67 Pa to give 1.75 g 1,1,1,3,3,6,6,6-octachloro-2-dichlorosilyl-1,3,6-trisilahexane (TCD- GC area 71.9%) as a mixture. 1H -NMR ($CDCl_3$, ppm): 1.53-1.59 (m, 4H, $SiCH_2CH_2Si$), 1.86 (s, 1H, SiH), 5.89 (s, 1H, SiH).

Example 5

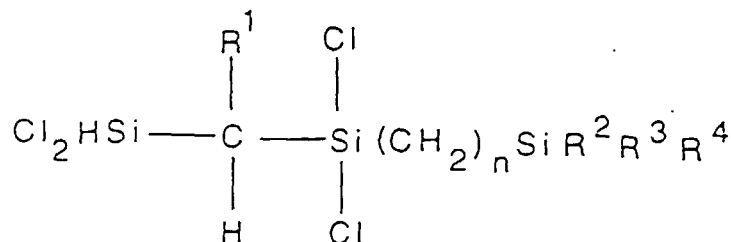
[0023] Hydrosilation of dichloromethylvinylsilane with bis(dichlorosilyl)dichloromethylsilylmethane. In the same apparatus as described in Example 1, 10 g of bis(dichlorosilyl)dichloromethylsilylmethane, 30 ml of dried benzene and 80 μ l of 0.1 M H_2PtCl_6 /IPA solution were placed. Then, to the flask were added 4 ml of dichloromethylvinylsilane and the flask content stirred for 15 minutes. The flask content was refluxed with stirring for 1 hour. Then, the flask content was vacuum distilled at 67 Pa to give 14.7 g of 2,2,4,4,7,7-hexachloro-3-dichlorosilyl-2,4,7-trisilaoctane (TCD-GC area 95.3%) as a mixture. 1H -NMR ($CDCl_3$, ppm): 0.84 (s, 3H, CH_2SiCH_3), 1.13 (s, 3H, $CHSiCH_3$), 1.33-1.58 (m, 5H, $CHSiCH_2CH_2Si$) 5.89 (s, 1H, SiH).

Example 6

[0024] Hydrosilation of trichlorovinylsilane with bis(dichlorosilyl)dichloromethylsilylmethane. In the same apparatus as described in Example 1, 10 g of bis(dichlorosilyl)dichloromethylsilylmethane, 30 ml of dried benzene and 80 μ l of 0.1 M H_2PtCl_6 /IPA solution were placed. Then, to the flask were added 3.89 ml of trichlorovinylsilane and the flask content stirred for 15 minutes. The flask content was refluxed with stirring for 2 hours. Then, the flask content was vacuum distilled at 67 Pa to give 15.2 g of 2,2,4,4,7,7,7-heptachloro-3-dichlorosilyl-2,4,7-trisilaheptane (TCD- GC area 94.5%) as a mixture. 1H -NMR ($CDCl_3$, ppm): 1.14 (s, 3H, $CHSiCH_3$), 1.56-1.60 (m, 5H, $CHSiCH_2CH_2Si$), 5.89 (s, 1H, SiH).

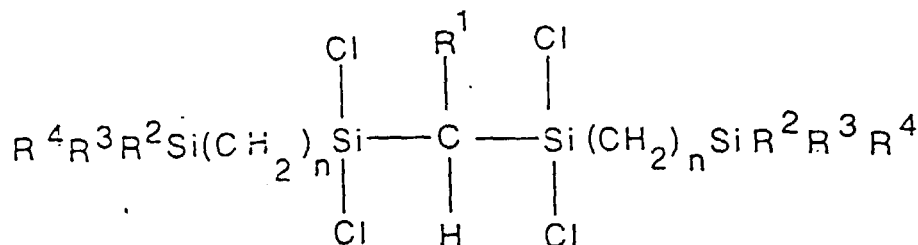
Claims

1. An organosilicon compound containing a silamethylene bond described by formula



where R^1 is selected from hydrogen, dichlorosilyl, trichlorosilyl, methyldichlorosilyl, dimethylchlorosilyl or trimethylsilyl, each R^2 , R^3 and R^4 are independently selected from hydrogen, chlorine and alkoxy radicals having 1 to 12 carbon atoms, aryloxy radicals having up to 12 carbon atoms, aryl radicals having up to 12 carbon atoms or saturated hydrocarbon radicals having 1 to 12 carbon atoms and $n=2$ to 6.

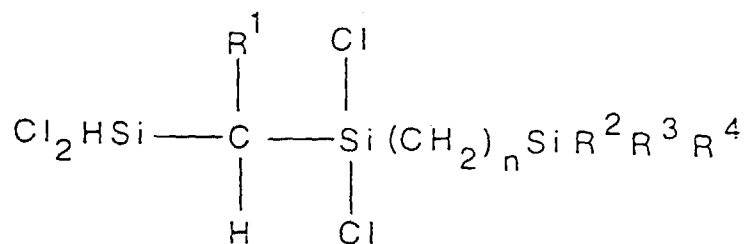
2. An organosilicon compound containing a silamethylene bond described by formula



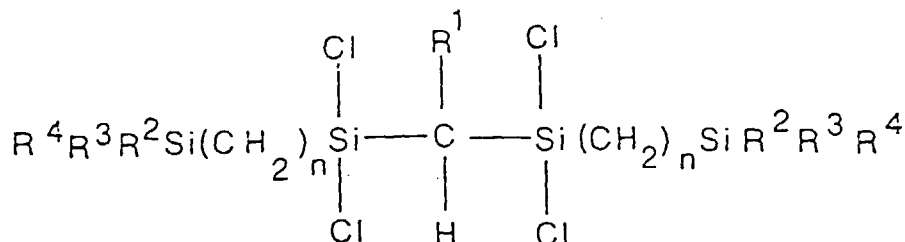
where R^1 is selected from hydrogen, dichlorosilyl, trichlorosilyl, methyldichlorosilyl, dimethylchlorosilyl or trimethylsilyl, each R^2 , R^3 and R^4 are independently selected from hydrogen, chlorine and alkoxy radicals having 1 to 12 carbon atoms, aryloxy radicals having up to 12 carbon atoms, aryl radicals having up to 12 carbon atoms or saturated hydrocarbon radicals having 1 to 12 carbon atoms and $n=2$ to 6.

3. An organosilicon compound according to Claims 1-2 where R^2 , R^3 and R^4 are independently selected from hydrogen, chlorine and methyl.

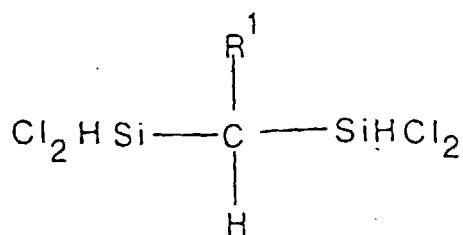
4. A method for making organosilicon compounds of Claims 1-3 described by formula



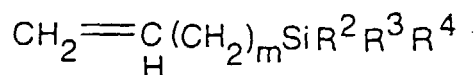
and



comprising effecting hydrosilation of a bis(dichlorosilyl)methane described by formula



with an unsaturated organosilane described by formula



in the presence of an effective amount of metallic hydrosilation catalyst, where R^1 is selected from hydrogen, dichlorosilyl, trichlorosilyl, methyldichlorosilyl, dimethylchlorosilyl or trimethylsilyl, each R^2 , R^3 and R^4 are independently selected from hydrogen, chlorine and alkoxy radicals having 1 to 12 carbon atoms, aryloxy radicals having up to 12 carbon atoms, aryl radicals having up to 12 carbon atoms or saturated hydrocarbon radicals having 1 to 12 carbon atoms and $m=0$ to 4.

5. A method according to Claim 4 where R^2 , R^3 and R^4 are independently selected from hydrogen, chlorine and methyl.
6. A method according to Claims 4-5 where the bis(dichlorosilyl)methane is selected from bis(dichlorosilyl)methane, bis(dichlorosilyl)trichlorosilylmethane or bis(dichlorosilyl)-dichloromethylsilylmethane.
7. A method according to Claims 4-6 where the unsaturated organosilane is selected from dichloromethylvinylsilane or trichlorovinylsilane.
8. A method according to Claims 4-7 further comprising the presence of an organic solvent.